Journal of Imaging Science and Technology® 50(4): 386–393, 2006.

Characterization of Various Development Centers in Silver Halide Photography

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Abstract. *In order to collectively study the factors influencing the developability of centers, the in situ measurement and analysis of the rate of development was made for various latent image centers and fog centers on AgBr grains with a variation of the kind of chemical sensitizations. The developability of these centers was analyzed from the viewpoints that the electron transfer from a developer to the electron-accepting level of a center should initiate the development, and that the height of the electron-accepting level of a center should be related to its size, chemical composition, band structure, the parity of the number of valence electrons in it, and the site for its formation. It was confirmed that the smallest developable center in AgBr emulsions was a fog center composed of two Au atoms while the smallest latent image centers in the emulsions with and without gold sensitization were Ag_2Au and Ag_4, respectively. The developabilities of these smallest centers were much smaller than those of larger ones. The developability of a center with a forbidden band as exemplified by Ag_2S (i.e., a fog center in a sulfur sensitized emulsion) was so small that several hundreds of nanoclusters per grain were needed to initiate the development of the grain.* © *2006 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2006)50:4(386)]

INTRODUCTION

Since development is one of the most essential processes in silver halide photography, it is important to characterize various development centers on the surface of silver halide grains. Such development centers include latent image centers formed under various conditions, Ag_2S and Ag clusters formed during digestions for sulfur sensitization and reduction sensitization (i.e., emulsion fog centers), and Ag clusters formed during development (i.e., developer fog centers).[1]

The developability of latent image centers also depends on the conditions of chemical sensitization and exposure. One of the most interesting points is a relationship between the developability and the size of development centers. Fayet et al.[2] studied the developability of size-selected silver cluster ions deposited onto AgBr microcrystals, and found that the smallest developable Ag cluster ion was Ag_4^+. Based on the simulation of the latent image formation with observed quantum sensitivity, Hailstone and others estimated that the smallest latent image centers consisted of three and four atoms in a sulfur-plus-gold (S+Au)-sensitized emulsion and a sulfur-sensitized emulsion, respectively, in terms of an abrupt developability criterion.[3] They also reported that the size of the actual latent image centers were widely distributed, and brought about the distribution of developability among them in such a way that smaller centers needed longer time for their development.[4]

The above result indicates the dependence of the developability on the chemical composition of development centers. Namely, the fact that the electronegativity of gold is larger than that of silver should provide the explanation for the estimated result that the smallest latent image centers formed in S+Au-sensitized emulsion and sulfur-sensitized emulsions were composed of three atoms (i.e., Ag_2Au) and four atoms (i.e., Ag_4), respectively, since it is expected that the replacement of a silver atom in a silver cluster by a gold atom should lower the electron-accepting level of the cluster and enhance its developability.

The rate of development depends on $\Delta E = E_{Ag} - E_{Dev}$, where E_{Ag} is the silver potential of latent image centers, and E_{Dev} is the redox potential of a developer. The value of E_{Ag} increases with increasing the developability of development centers. The developability of latent image centers should influence the progress and rate of development. The rate of development should depend on the rate of the reaction taking place at the surface of a center when the rate of the reaction is slow, while it should depend on the rate of the diffusion of the species involved in the reaction when the rate of the reaction is sufficiently high.

There are two limiting cases for the progress of development. The amount of developed silver in an emulsion layer is proportional to the amount of developed silver in each grain in one extreme type (A) and to the number of fully developed grains in the other extreme type (B). Types A and B are called parallel and granular developments, respectively.[5] In the case of parallel development, the developability of latent image centers is so high that the development of all the grains is initiated nearly simultaneously at the beginning of development, and that the rate of development is determined by the growth of developed silver. In the case of granular development, the developability of latent image centers is so small that the rate of development is determined by the time needed for the initiation of development by latent image centers.

As stated above, the phenomena relating to photographic development widely varied, depending on the kind

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Received Apr. 28, 2005; accepted for publication Jan. 8, 2006.
1062-3701/2006/50(4)/386/8/$20.00.

of development centers and the condition of development. It is therefore meaningful to explain the development phenomena from such unified point of view as shown below. In the first place, the profile of the progress of development as initiated by various development centers were measured and analyzed by use of the method, which one of the authors has developed on the basis of the measurement of the change in absorbance of a silver halide emulsion layer at wavelength of 1090 nm during development.[6]

Second, the phenomena thus observed were analyzed from the viewpoint that the developability of a development center depended on the height of its electron-accepting level, i.e., electron affinity, since the electron transfer from a developer to the electron accepting level of the center initiated the development. It is therefore helpful for our understanding of the behavior of development centers to explain the developability of these development centers from the viewpoint of the height of their electron accepting levels, by taking into account the fact that the electron accepting levels of centers depend on their size, chemical composition, band structure, the parity of the valence electrons, and sites for its formation.

EXPERIMENT AND THEORY

Two kinds of photographic emulsions were prepared by a controlled double jet method.[7] They were prepared at *p*H 5.0 and *p*H 2.0, and composed of octahedral AgBr grains with average equivalent diameter of 0.47 and 0.20 μm, respectively. The equivalent diameter is a diameter of a sphere whose volume is the same as that of the grain and was determined by electron microscopy. The *p*Ag and *p*H of these emulsions were adjusted to be 8.4 and 6.5 at 40 °C, respectively, before coating.

These emulsions were subjected to digestions for 60 min at 60 °C in the presence of $Na_2S_2O_3 \cdot 5H_2O$ for sulfur sensitization, in the presence of $Na_2S_2O_3 \cdot 5H_2O$, $HAuCl_4$, and KSCN for S+Au sensitization, and in the presence of aminoiminomethanesulfinic acid (AIMA) or dimethylamineborane (DMAB) for reduction sensitization. The amounts of these sensitizers were adjusted to achieve the highest sensitivity on exposure for 10 s.

These emulsions were coated on cellulose triacetate film bases. The coated emulsions were exposed to a tungsten lamp (color temperature 2854 K) through a continuous wedge and a blue filter. The development of exposed emulsion coatings was carried out by use of an MAA-1 developer.[8] Photographic sensitivity of each emulsion layer was given by the reciprocal of the exposure required to give optical density of 0.1 above fog density.

The developability of various centers was estimated from the rate and its activation energy of the development initiated by them. The rate of development was obtained as the reciprocal of the time needed to give 10% of the maximum density. Since it was difficult to measure exactly the rate of the slow development in the presence of the fast development, the rate of the slow development was measured only in the absence of fast development.

The change in the fraction of developed grains in an emulsion layer was given by the change in its optical density at 1090 nm i.e., Infrared (IR) density. The IR density was measured by use of a multichannel photodiode system (MCPD-100 or 1000 made by Photal Co., Ltd., Tokyo, Japan) as described in the previous paper.[6] The IR density arose from the light absorption of developed silver and the light scattering by undeveloped silver halide grains. It was confirmed in the previous paper[6] that the density due to the light absorption of developed silver at 1090 nm was proportional to the amount of developed silver, which was measured by means of x-ray fluorescence analysis, for the primitive, sulfur-sensitized, and sulfur-sensitized AgBr emulsions on exposure to light at the shoulders of their characteristic curves with variation of the time of development. Since those emulsions and experimental conditions were the same as those in this study, the above-stated proportionality should be also valid for the experiments in this study.

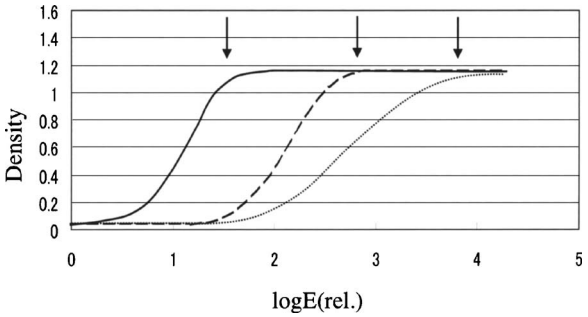

Figure 1. Characteristic curves of emulsion layers composed of octahedral AgBr grain with average diameter of 0.47 μm. The emulsions were primitive (dotted line), sulfur sensitized (dashed line), and S+Au-sensitized (solid line). Each sample was exposed for 10 s and developed by use of an MAA-1 developer at 30 °C for 5 min. The arrows in the figure indicate the shoulder exposure levels for the above-stated emulsions.

RESULTS

Developability of Latent Images Centers

The characteristic curves of primitive, sulfur-sensitized and S+Au-sensitized emulsion layers with octahedral AgBr grains of 0.47 μm are shown in Fig. 1. The arrows in the figure indicate the shoulder exposure, which was regarded as the threshold to render all the grains in the coated sample developable. The development profiles of the latent image centers formed at various exposure levels in the primitive, sulfur-sensitized and S+Au-sensitized emulsion samples are shown in Fig. 2.

In the case of the primitive sample [Fig. 2(a)], the development proceeded rapidly through a single step with the same rate at every exposure level. This result indicated that the developabilities of almost all the latent image centers formed on the primitive grains were already large enough to complete the development within 30 s according to the method described in the previous section.

The development profile of the sulfur sensitized sample [Fig. 2(b)] exhibited two steps at low exposure level. It is judged from Fig. 2 that each development profile mainly

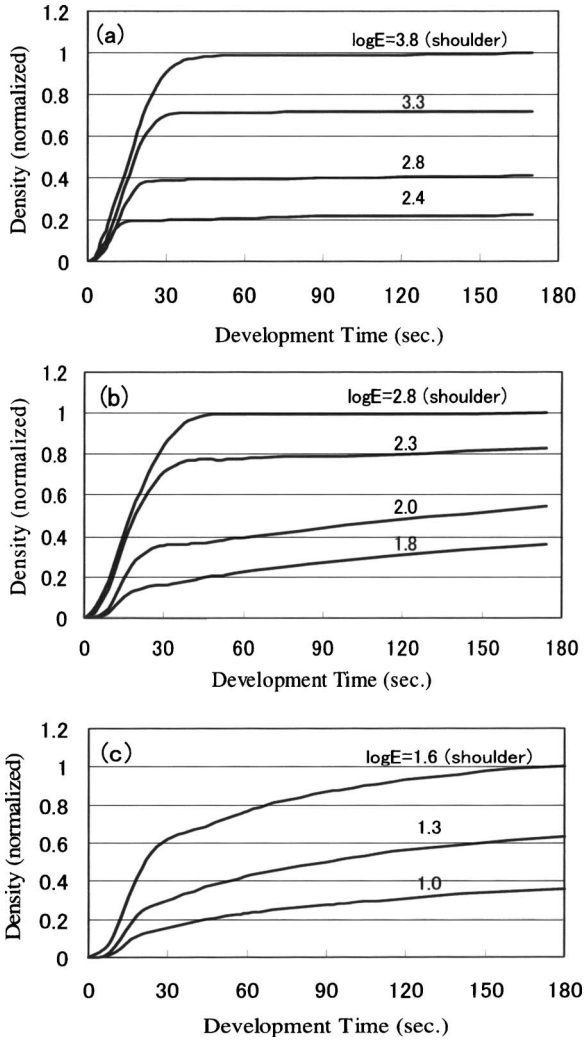

Figure 2. Increase in IR density as a function of development time for primitive emulsion layers (a), sulfur sensitized emulsion layers (b), and S+Au-sensitized emulsion layers (c), which were exposed for 10 s through neutral filters with variation of optical density. The relative exposure is indicated on each curve in the figure. Development was carried out in an MAA-1 developer at 30 °C.

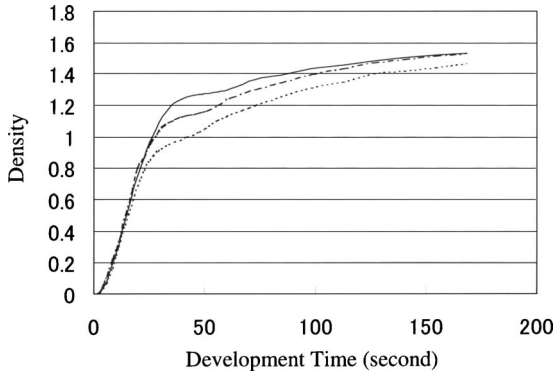

Figure 3. Effect of postexposure on the fast component in the development profile of a S+Au-sensitized emulsion layer. A dotted line represents the development profile of an emulsion layer, which was exposed for 10 s at its shoulder level. The post exposure was carried out for 1000 s at relatively low (dash-dotted line) and high (solid line) intensities, respectively. The development of these films was carried out at 30 °C in an MAA-1 developer.

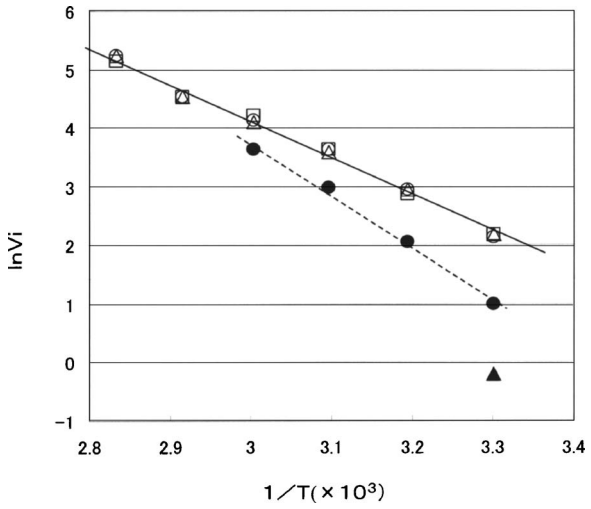

Figure 4. Temperature dependence of the rate of development Vi of primitive (□), sulfur sensitized (△, ▲) and S+Au-sensitized (○, ●) emulsions. Open and closed symbols represent the results for the fast and slow components, respectively.

consisted of two components. These two components were already recognized and analyzed in the previous paper.[6] Taking into account these results and this knowledge, the authors considered that the existence of latent image centers with different developability should be the most probable cause for the appearance of two steps in the development profile.

In this paper, these two steps are named the fast and slow developments, and defined as the development completed within 30 s and that prolonged for more than 30 s, respectively, under the condition of the experiments in this study. The fraction of the slow component decreased with increasing exposure and disappeared at the shoulder exposure. The development profile of the S+Au-sensitized sample [Fig. 2(c)] showed significant fraction of the slow component even at the shoulder exposure. The fraction of the slow component was reduced by post exposure, as shown in Fig. 3.

The temperature dependence of the rate of development is shown in Fig. 4. The slopes of the straight lines gave the activation energies, which were 12.2 and 17.7 kcal/mol for the fast and slow components, respectively. The rate and activation energy of the fast component were the same among different emulsions, while those of the slow component differed significantly among different emulsions.

It was reported that two types of reduction sensitization centers brought about an increase in sensitivity. One of them acts as a positive hole trap and is named an *R* center, while the other acts as an electron trap and is called a *P* center.[9] The behaviors of the two types of reduction sensitization centers formed by use of two kinds of reduction sensitizers on octahedral AgBr emulsion grains are shown in Fig. 5, indicating them to be independent of the kind of sensitizer. The amount of reduction sensitizers were controlled to form mostly *R* centers (emulsion A) and to form both *R* centers

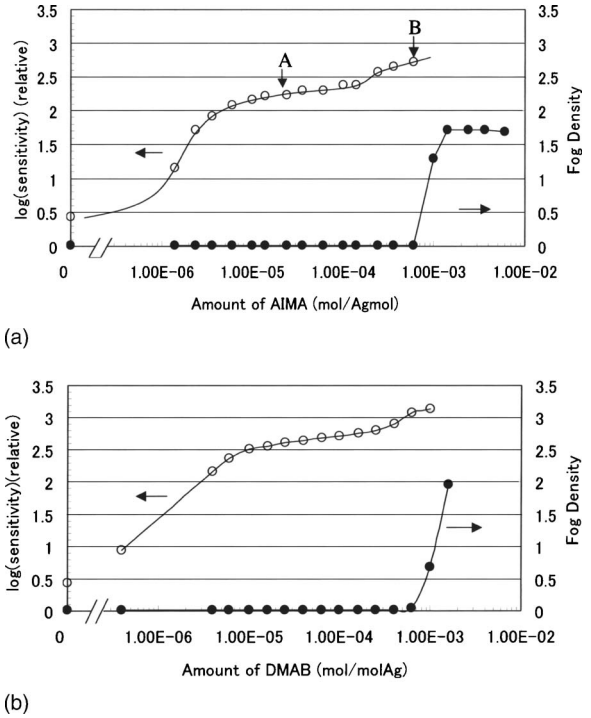

Figure 5. Photographic sensitivity (○) on exposure for 100 s and fog density (●) of reduction sensitized emulsion layers composed of octahedral AgBr grains with average diameter of 0.2 μm as a function of the amount of AIMA (a) and DMAB (b). The development of these emulsion layers was carried out at 30 °C by use of an MAA-1 developer.

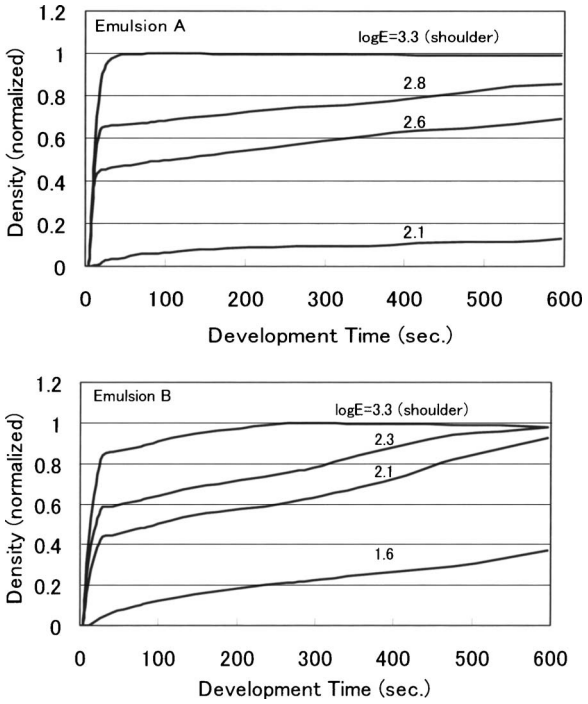

Figure 6. The IR density as a function of development time of the reduction sensitized emulsions A and B as indicated in Fig. 5, which was exposed for 10 s with a variation of exposure. The relative exposure is indicated on each curve in the figure. The development of the exposed emulsion layers was carried out at 30 °C by use of an MAA-1 developer.

and *P* centers (emulsion B). Since unexposed reduction sensitized emulsions did not give rise to any increase in density on development, it is obvious that both *R* and *P* centers had no developability under ordinary development condition.

Figure 6 shows the development profiles of the reduction sensitized emulsions as a function of exposure. The slow component was slightly observed in the development profile of emulsion A on low exposure, and disappeared at the shoulder exposure. The slow component in emulsion B was observed more explicitly than that in emulsion A, and did not disappear even at the shoulder exposure.

Developability of Fog Centers

The fog density of the reduction sensitized octahedral AgBr emulsion in the presence of various amounts of gold ions is shown in Fig. 7. Similar results were observed with the cubic emulsion. The addition of gold ions as $HAuCl_4$ to the reduction sensitized emulsion converted some of reduction sensitization centers into fog centers. It should be noticed that the fog density increased, reached a maximum, and then decreased with the amount of DMAB when the added amount of $HAuCl_4$ was fixed and limited. The development of all the fog centers formed under the condition indicated by the arrow in Fig. 7 proceeded slowly, as shown in Fig. 8, indicating that they did not correspond to any large centers.

As shown in Fig. 7, excessive reduction sensitization treatment caused the formation of fog centers composed of Ag clusters (i.e., reduction clusters), while the photolysis of

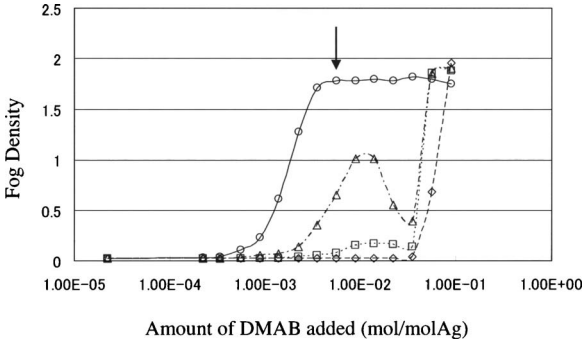

Figure 7. Fog density of reduction sensitized emulsion layers composed of octahedral AgBr grains with average diameter of 0.2 μm as a function of the amount of DMAB added. They contained $HAuCl_4$ and KSCN of 0 and 0 mmol/mol AgBr (◇), 0.22 and 0.92 mmol/mol Ag (□), 0.54 and 2.3 mmol/mol Ag (△), and 3.4 and 14 mmol/mol Ag (○). The development of these emulsion layers was carried out at 20 °C for 10 min by use of an MAA-1 developer.

silver halide results in the formation of light clusters. It was reported[10,11] that the number of reduction clusters with diameter of ~5 nm on the average was 200 per grain, while only one light cluster with diameter of ~5 nm on the average was present on a grain. Nevertheless, it was confirmed that the development of the former grains was slower than that of the latter grains in accord with the previous paper[11] and the work of Hamilton and Baetzold.[12]

Fog centers were also formed by sulfur sensitization treatment with an excessive amount of sensitizer, giving rise

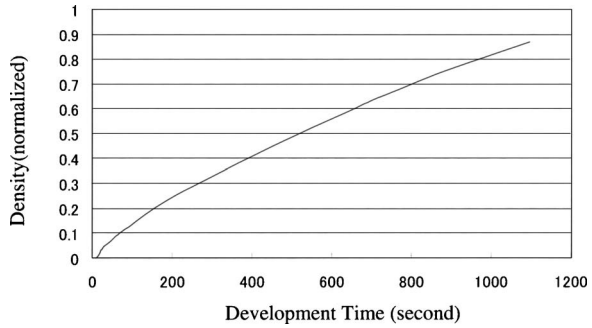

Figure 8. Change in IR density as a function of development time of the emulsion layer indicated by an arrow in Fig. 7. The development of this emulsion layer was carried out at 20 °C by use of an MAA-1 developer.

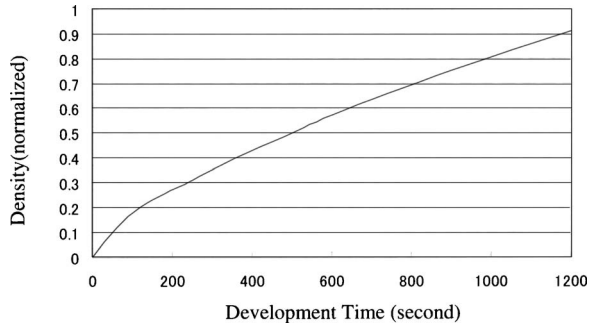

Figure 9. Change in IR density of an excessively sulfur sensitized emulsion layer as a function of development time. The development of this emulsion layer was carried out at 30 °C by use of an MAA-1 developer.

to the absorption band which extended into the wavelength region beyond 760 nm as described in the previous papers.[13,14] They were ascribed to Ag_2S clusters with size of several nanometers, consisting of 50–100 Ag_2S units. Their development profile, as shown in Fig. 9, indicated that their developability was very low.

It is known that there are two types in fog, i.e., emulsion fog and developer fog. The latter has been analyzed and reported elsewhere.[15]

DISCUSSION

Electron Transfer Process

Since the electron transfer from a developer to a development center initiates the photographic development process, it is expected that the development process is explained reasonably on the basis of the Marcus theory, according to which the rate constant increases, reaches a plateau, and then decreases to give the inverted region, with increasing a free energy change of a reaction.

However, it is usually difficult to study the development process in terms of its rate constant,[16] since a development process may be too complicated to be fit to a rate law in order to obtain the rate constant. In addition, it is not always easy to obtain the free energy change of a development process. The literature[17] and also the present study have not indicated any conditions under which the rate of development decreases with increasing the gap in free energy or enthalpy for the development process. It is therefore considered that the inverted region is absent in the development process. It is known in the field of spectral sensitization in silver halide photography that the inverted region does not appear in the electron transfer from a molecule or an ion to the substances having many electron-accepting levels with high density.[18] By taking into account the observation by Tasaka et al.,[10] we propose that a latent image center which brings about the development with diffusion limited rate in an ordinary developer should be large enough to have many electron accepting levels with high density.

This consideration is not in contradiction with the idea that photographic development takes place as a result of the electron transfer from a developer to a development center according to the Marcus theory. Accordingly, the present authors have tried to systematically characterize various development centers within the framework of the Marcus theory in terms of a common factor, i.e., the electron accepting levels of the centers, although it must be admitted that the energy assigned to the lowest electron accepting level, i.e., electron affinity of the center, is not a free energy, but an enthalpy, and that free energy and enthalpy are related by an entropy, i.e., the density of states in the centers.

The height of the electron accepting levels of a development center depends on its size, chemical composition, parity of the number of valence electrons, site for its formation, and band structure. Accordingly, the results described in the previous section are reviewed from the viewpoints of the above factors.

Size of a Center

It is generally considered that the electron affinity of centers increases with increasing their size, approaching that of bulk silver (i.e., −4.3 eV below the vacuum level), and that the developability of image centers increases as the energy of their electron accepting level is lowered.

From the viewpoint of developability, the present study has clarified that stable image centers are classified into three groups; centers without developability (i.e., latent subimage centers), those with weak developability (i.e., small latent image centers), and those with strong developability (i.e., large latent image centers). Although the developability should increase monotonically with increasing size of the centers, the rate of development eventually becomes independent of the developability and determined by the rate of the diffusion of chemical species involved as the size of centers increases.

The rate of development initiated by small latent image centers is small, giving the slow component in the development profile. On the other hand, the rate of development initiated by large development centers is large and independent of their size, giving the fast component in the development profile.

We further propose that the progress of the development initiated by large latent image centers is large enough to be diffusion limited and parallel,[5] since its rate was dependent neither on the kind of emulsions nor on the exposure condition. Although the activation energy of the rate of

the fast development in this study (i.e., 12.2 kcal/mol) was larger than reported for the diffusion of developing agents (i.e., 3–7 kcal/mol),[16,19] the latter should be strongly dependent on the concentration of gelatin in a swollen emulsion layer in a developer. It was reported that the observed values of the activation energy of the diffusion hydroquinone were 3.7 and 8.0 kcal/mol in swollen layers with gelatin concentration of 10% and 20%, respectively.[20] On the basis of this tendency and the fact that the gelatin concentration in an emulsion layer in a developer in this study was of the order of ~50%, it is considered that the observed activation energy for the fast development in this study is not in contradiction with the idea that the fast development is diffusion limited. On the other hand, the progress of the development initiated by center was so small as to be reaction limited and granular.[5,6]

This consideration was also supported by the observation that uniform postexposure decreased the fraction of the slow component observed in the development profile of an S+Au-sensitized emulsion. Since the postexposure lets electron trapping silver clusters grow, it follows that the difference in the rate of development between the slow and fast components may be due to the difference in size between the latent image centers giving rise to these components.

On the basis of the results in the previous and present studies, we conclude that the centers which gave the slow component in the development profile were small latent image centers, whose size was close to that of the smallest ones. The size of development centers formed on a S+Au-sensitized emulsion was estimated on the basis of the nucleation and growth (N&G) model for latent image formation developed by Hamilton.[21] In this procedure, the probabilities of nucleation and the recombination between a photoelectron and a positive hole in the emulsion were determined so that the simulation could reproduce both the quantum sensitivity and reciprocity law failure of the emulsion.

The characteristic curve simulated for S+Au-sensitized emulsion under the assumption that the smallest latent image center consisted of five atoms was coincident with the curve obtained by the development for 30 s [i.e., the fast component of the development profile in Fig. 2(c)], and the characteristic curve simulated under the assumption that the smallest latent image center consisted of three atoms was coincident with that obtained by the development for 30 min [i.e., including the slow component of the development profile in Fig. 2(c)]. The simulated characteristic curves and observed ones are shown in Fig. 10. This result suggests that the slow component in the development profile was due to latent image centers composed of three and four atoms in S+Au-sensitized AgBr emulsions, and that the fast component was due to latent image centers composed of five and more than five atoms.

The results reported by Fayet[2] and Hailstone et al.[3(b)] and those obtained in this study indicated that the smallest latent image centers formed in S+Au-sensitized and sulfur sensitized emulsions were clusters consisting of three and four atoms, respectively. Figure 11 shows the result of the simulation on the basis of the N&G model, which indicates the relation between the characteristic curve and the size of the smallest development center. The characteristic curve of the S+Au-sensitized emulsion depended on the size of the smallest latent image centers, while that of the primitive emulsion did not. In the light of the fact that only one latent image center was formed on each grain, this result indicates that the fraction of the smallest latent image centers among latent image centers formed was negligible in the primitive emulsions, whereas it was substantial in the S+Au-sensitized emulsion. The difference arose from the fact that the growth probability of a latent image center is relatively large compared with the probability of nucleation in the primitive emulsion[10] and that the number of photoelectrons (i.e., absorbed photons) available for the growth of a latent image center was much larger in the primitive emulsion than in the S+Au-sensitized one as indicated by the difference in quantum sensitivity between them.

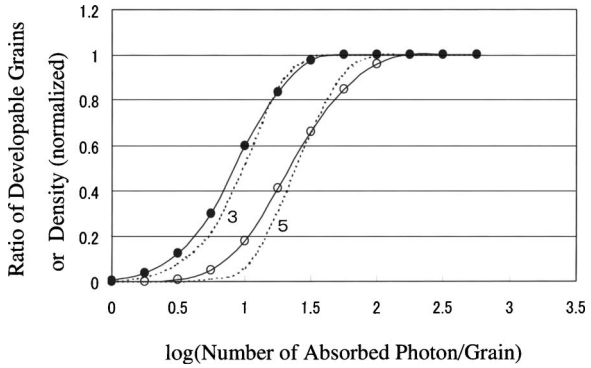

Figure 10. Comparison of experimental characteristic curves (solid lines) with simulated ones (dotted lines). Experimental curves were for S+Au-sensitized emulsion layers, which were exposed for 10 s and developed at 30 °C for 30 s (○) and 30 min (●) by use of an MAA-1 developer. Simulated curves were based on the N&G model (see Ref. 27), where the probabilities of nucleation η and recombination ω were 0.5 and 1.0, respectively. The numbers in this figure indicate the numbers of atoms in the smallest latent image centers (see Ref. 6).

Chemical Composition of a Center

As described in the Introduction, it is already known that the replacement of a silver atom in a silver cluster by a gold atom lowers the electron accepting level of the cluster and enhances its developability owing to the fact that the electronegativity of gold is larger than that of silver. This knowledge is useful to prove the idea that a Au_2 cluster is the smallest development center.

Although Hamilton and Logel indicated that a Au_2 cluster formed on SiO_2 could initiate physical development,[22] we are not sure that a Au_2 cluster on a Ag*X* grain really initiates chemical development and may be regarded as the smallest development center among those ever reported in the literature. This question could be examined by the following considerations on the basis of the results obtained in this study.

As seen in Fig. 12, the addition of gold ions to a reduction sensitized emulsion rendered a silver dimer developable

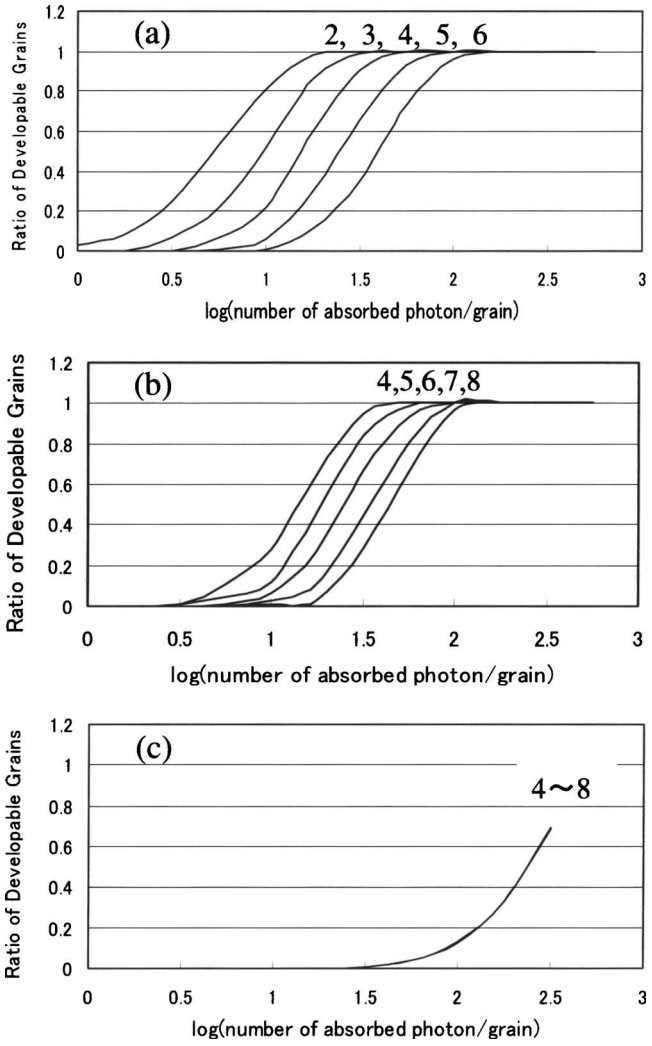

Figure 11. Sets of the characteristic curves simulated for a S+Au-sensitized emulsion layer [(a) η=0.5], sulfur sensitized one [(b) η=0.1], and primitive one [(c) η=0.0033] on the basis of the N&G model (see Ref. 27). The numbers in this figure correspond to the number of atoms in the smallest latent image center.

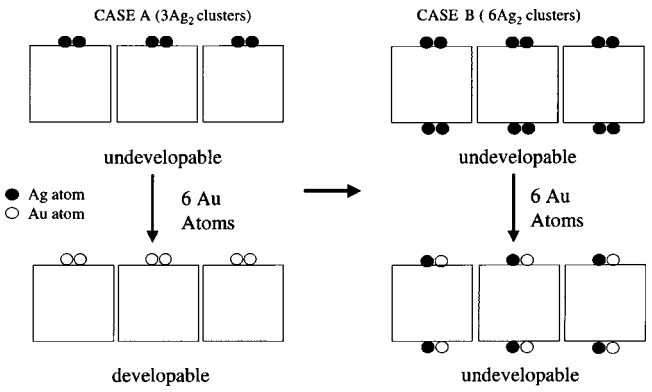

Figure 12. Illustration showing the replacement of a Ag atom in a Ag_2 by a Au atoms in a reduction sensitized emulsion with the presence of a fixed amount of gold ions. If the number of Ag_2 is small, at least one of Ag_2 on a grain can be transformed to an Au_2 to make the grain developable (case A). If the number of Ag_2 is large, it is probable that any of Ag_2 on a grain is not transformed into a Au_2, leaving the grain undevelopable (case B).

and thus converted it into a fog center. When the amount of gold ions was fixed and limited, the fog density increased, reached a maximum, and then decreased with increasing the amount of a reduction sensitizer. This result indicates that two or more gold ions are needed to render a Ag dimer developable, as opposed to the attachment of a Au atom to a Ag dimer, since a resultant Ag_2Au center should be identical to the smallest latent image center and therefore developable. It is also noted that the fog centers formed under the condition indicated by an arrow in Fig. 7 do not contain any large center responsible for the fast component in the development profile. We therefore conclude that the fog center thus formed was a Au dimer.

Band Structure

The lowest unoccupied electronic energy level and the highest occupied one in a metal cluster are close to each other, while they are widely separated from each other in a semiconductive cluster owing to the presence of the forbidden band in it. It is also known that the band gap between the conduction band and the valence one of a semiconductor increases with decreasing its size owing to the quantum-size effect.[23]

As described and analyzed in the previous paper,[14] the fog centers formed during excessive sulfur sensitization treatment exhibited several properties similar to those of Ag_2S, and were ascribed to Ag_2S clusters with diameter of several nanometers. It is therefore considered that a semiconductor cluster has a higher electron accepting level and smaller developability than a metal cluster, which could explain why excessive sulfur sensitization treatment formed fog centers, which are composed of Ag_2S and have low developability even when they were as large as several nanometers.

A rough estimation of their electron accepting level is given as follows. As reported in the previous paper,[14] the absorption band of the fog centers composed of Ag_2S was observed around 760 nm (i.e., ~1.6 eV). The bottom of the conduction band and the top of the valence band of AgBr are 3.6 and 6.0 eV, respectively, below the vacuum level.[24] When the Fermi levels of the center and a AgBr grain were at their middle points in their forbidden bands and coincided with each other on contact, we judge that the bottom of the conduction band of the center was ~4.0 eV below the vacuum level, higher than the electron accepting level of Ag, which is 4.3 eV below the vaccum level.

Developability of Latent Image and Fog Centers

It is generally described in the literature that the developability of latent image centers is larger than that of fog centers.[20] Hamilton and Baetzold demonstrated without any clear explanation that this was the case even for the arrested development of the centers composed of nanoparticles of silver.[12] It is therefore meaningful to analyze the difference in developability between latent image and fog centers from the viewpoint of the present study.

Latent image centers are mainly composed of silver, while fog centers are usually composed of silver or silver sulfide. The reason for weak developability of a fog center

composed of silver sulfide was analyzed in the previous section. The reasons for weak developability of a fog center composed of silver may be the parity of the number of valence electrons in it and the site for its formation, as discussed below.

Since an odd cluster, which contains odd number $(2n+1)$ of valence electrons, has a singly occupied molecular orbital (SOMO) whose energy level is lower than that of lowest unoccupied molecular orbital (LUMO) of an even cluster, which contains even number $(2n+2)$ of valence electrons, the electron accepting level of the former is deeper than that of the latter.[25]

In the former paper,[11] it was indicated that almost all the reduction clusters were even clusters, while the population of light clusters contained many odd clusters. In the light of Kubo's theory, this conclusion was supported by the following experimental result and considerations. Namely, the magnetic susceptibility of a reduction cluster with diameter of ~5 nm was negligibly small (~1/1000) as compared with that of a light cluster with similar diameter. Since the energy required for the acceptance or release of an electron by a cluster with diameter of 5 nm is as high as 0.4 eV, the number of the valence electrons in the cluster hardly changes after it is formed. In addition, the spacing of the adjacent energy levels Δ in the cluster was much larger than the Zeeman energy splitting of the spin-up and the spin-down states at *X*-band frequencies used for electron spin resonance (ESR) measurements.

It is, however, noted that Δ was judged to be 0.001 eV,[11] and was not large enough to account for the difference in the activation energy of development between light and reduction clusters (i.e., 0.001–0.06 eV depending on the kind of developer) and attribute it simply to the difference in the parity without taking into account the idea that the sites, at which the light and reduction clusters were formed, were different from each other.

As indicated in the previous paper,[9] reduction clusters were formed at neutral kink sites more easily than at positively charged kink sites, while light clusters are preferentially formed at positively charged kink sites. The electronic energy levels of clusters at positively charged kink sites should be lower than those of clusters at neutral kink sites owing to the following two reasons. (1) The influence of the positive charge on the electronic energy levels in a cluster. (2) The coordination of electrons in a center to a silver ion at a positively charged site, as proposed previously.[26] It is therefore considered that the difference in developability between the light and reduction clusters with diameter of ~5 nm was ascribed to the difference in the nature of their sites for formation in addition to the difference in parity between them.

CONCLUSION

The rate of development was measured in situ and analyzed for various development centers in order to study the factors contributing to their developability. The developability of centers could be explained in terms of the height of their lowest electron accepting level (electron affinity) from the viewpoint of the fact that the electron transfer from a developer to the electron accepting level of a center should initiate development. The electron affinity of a center depends on its size, chemical composition, band structure, the parity of the number of valence electrons in it, and its lattice site.

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